

Spin-asymmetric graphene nanoribbons in graphane on silicon dioxide

M. Ijäs^{1,*}, P. Havu¹, A. Harju¹, and P. Pasanen²

¹*Department of Applied Physics and Helsinki Institute of Physics, Aalto University, FI-02150 Espoo, Finland*

²*Nokia Research Center, P.O. Box 407, Helsinki FI-00045 Nokia Group, Finland*

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Hydrogenated graphene, graphane, is studied on oxygen-terminated silicon dioxide substrate using *ab initio* calculations. The two lowest-energy structures with quarter and half mono-layer hydrogen coverage are presented. We form zigzag graphene nanoribbons by selectively removing hydrogens from the epitaxial graphane layer. In these ribbons, the spin degeneracy of the freestanding antiferromagnetic zigzag ribbons is broken, and band gaps of different magnitude emerge for the opposite spin species. This degeneracy breaking is due to a charge imbalance in the substrate below the ribbon, introduced through the asymmetric alignment of the substrate atoms with respect to the edges of the graphene ribbon. As the edge geometry is restricted by the neighboring graphane, the zigzag edges are robust to reconstructions suggested to destroy edge magnetism in freestanding graphene ribbons.

Ever since the first experimental discovery of graphene and its extraordinary electronic properties [1], the search for practical applications for this new material has been intense. As the lack of a band gap is a hindrance for many applications, various methods have been suggested to induce a gap, among them cutting the material into thin stripes, graphene nanoribbons (GNRs), that have a width- and edge-dependent gap [2]. In addition, due to the antiferromagnetic spin alignment between the ribbon edges, zigzag graphene nanoribbons (ZGNR) show potential as spin filters [3]. In the presence of an external electric field across the ribbon width, they are predicted to turn into half-metals [4, 5], one of the spin channels being insulating and the other metallic. The halfmetallicity might be facilitated by different edge-terminating groups [3, 6] and chemical doping by boron and nitrogen [7–9].

The existence of a graphene derivative, the fully hydrogenated graphane, was first theoretically predicted as late as in 2007 [10] and also experimentally verified soon after that [11, 12]. Freestanding graphane, with hydrogenation on both sides of the graphene layer, has been theoretically predicted to be energetically stable [10], unlike one-sided hydrogenation [13, 14]. In the experimental fabrication procedures, like exposure of a graphene layer deposited on a substrate to atomic hydrogen [12] or hydrogen plasma [11], it is unlikely that the hydrogenation occurs on both sides.

For both graphene and graphane, the effect of a substrate has widely been neglected in theoretical works, where focus has been on modeling of freestanding graphene. Silicon dioxide is a likely substrate candidate as it is insulating, cheap, and widely-used in the current technologies. The previous studies of graphene on SiO₂ [15–17] are contradictory whether or not graphene-substrate bonds are formed. To the best of our knowledge, graphane on a substrate has not been studied. For simplicity, the one-sidedly hydrogenated graphene layer on a substrate is called graphane in this work (also the

name "graphone" has been used in the literature [13]).

An interesting suggestion is that graphene nanoribbons could be drawn in graphane by selective dehydrogenation [18]. Dehydrogenation using an STM tip has been experimentally demonstrated [19]. Theoretical calculations [18, 20] predict that the properties of graphene nanoribbons embedded in freestanding graphane are very close to those of freestanding nanoribbons. The effect of the substrate on such nanoribbons is, however, not known. The main topic of our letter is to study graphene nanoribbons formed in graphane on SiO₂. We show that the ribbons show interesting electronic structure with spin-asymmetric bands due to the interaction with the substrate. Moreover, the neighboring graphane restricts edge reconstructions predicted [21, 22] to destroy edge magnetism in freestanding GNRs.

The *ab initio* calculations were performed using density-functional theory with a van der Waals (vdW) correction [23], implemented in the all-electron FHI-aims code [24]. For computational details, see Ref. [25]. Silicon dioxide bulk in the α -phase was modeled using slabs whose thickness was three unit cells corresponding to a layer of 15.8 Å. As periodic boundaries were used for all directions, vacuum layer of approximately 20 Å was placed between adjacent slabs. A graphene layer with an optimized unit cell volume at the distance of 2 Å from the O-terminated SiO₂ (0001) surface was placed on both sides of the SiO₂ slab and the carbon atoms and three uppermost atoms of the substrate were relaxed. The two interfaces on opposite sides of the slab were equivalent. The mismatch between the lattice vectors of graphene and the substrate was small, only 1.3%.

To briefly compare our results for the graphene-silicon dioxide system to previous works [15–17], we note that in our calculations, graphene does not form bonds with the substrate atoms. This result is in agreement with calculations of Ao *et al.* [16] but in contradiction to previous results by Kang *et al.* [15] and those of Shemella and Nayak [17], who found carbon-oxygen bonds in all cases

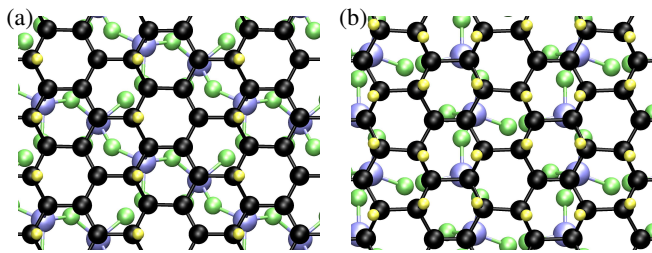


FIG. 1. (Color online) The two lowest-energy configurations for graphane on the O-terminated face of SiO_2 . (a): The quarter-hydrogenated case (b): The half-hydrogenated case. Carbon atoms are black, other atoms from small to large: hydrogen, oxygen, and silicon

studied except in the case of a hydrogen-saturated surface with terminating OH groups. The neglect of vdW forces in their calculations does not explain this discrepancy, as vdW provides additional attraction. However, during the structural relaxation we have observed geometries with fairly small residual forces that show carbon-oxygen bonding, possibly explaining the discrepancy.

For determining the lowest-energy hydrogen atom configurations on graphane, one to six hydrogen atoms per unit cell containing eight carbon atoms were placed initially either on the graphene carbon atoms or between them, corresponding to $1/6$ – $3/4$ hydrogen mono-layers (ML). In scanning of a large number of structures, the SiO_2 layer was reduced to one unit cell corresponding to 5.5 \AA . The system was allowed relax the carbon and hydrogen atoms. For the lowest-energy structures, calculations were confirmed by using the thicker slab with three SiO_2 unit cells and additionally relaxing three layers of the substrate atoms closest to the surface. Altogether 492 initial hydrogen atom configurations were considered. A detailed analysis on the results is left for later work and we present here only results relevant for the nanoribbon calculations.

The two most stable graphane configurations, with $1/4$ ML and $1/2$ ML hydrogen coverage in the eight-carbon unit cell, are shown in Fig. 1. In the first configuration, the hydrogen atoms form lines along the zigzag chains with a hydrogen atom on every second carbon atom and a free carbon chain between two adjacent hydrogenated chains. On the hydrogenated rows, the carbon atoms without hydrogen bind to the substrate. In the second configuration, hydrogen atoms reside on all zigzag lines but unlike in freestanding graphane hydrogenated on both sides, they are on both sublattices, forming groups of four hydrogen atoms that are slightly tilted towards each other. The two carbon atoms in the middle of each group bind to a SiO-pair underneath. The distance between the uppermost substrate atoms and the closest atoms is almost the same for both configurations, 1.41 \AA and 1.40 \AA , respectively. We could not find a stable configuration for free-standing graphane that is

hydrogenated only on one side.

Both configurations are semiconductors but their band gaps differ considerably. The quarter-hydrogenated configuration in Fig. 1(a) has only a minigap of 0.04 eV whereas the magnitude is 3.1 eV for half-hydrogenated graphane of Fig. 1(b). The band gap of graphane has not been experimentally measured but for graphane on iridium, a lower limit of 0.5 eV has been found [26]. The gap calculated here is, of course, merely the Kohn-Sham gap that is known to underestimate the real gap in LDA and GGA calculations. The use of the GW self-energy correction could improve the prediction and in the double-sided freestanding graphane the band gaps increases by approximately 2 eV to 5.4 – 6.0 eV [27, 28].

We choose the half-hydrogenated version as a starting point for our ribbon simulations, although the quarter-hydrogenated structure is lower in energy. Our calculations are performed at $T = 0 \text{ K}$ and in vacuum. Depending on the hydrogenation conditions, the more densely hydrogenated structure could be formed (see the thermodynamics-based analysis by Wassman *et al.* [21] on the stabilities of different GNR edge hydrogenations). In the experiment, hydrogen atoms on graphene tend to cluster forming denser structures [26] and we intend to model a ribbon drawn through such an area. Additionally, the band gap in the half-hydrogenated configuration is larger and its structure allows the formation of ribbons with smoother edges, in the fashion of earlier calculations on freestanding graphene-graphane ribbons [18, 20].

The GNRs are formed by removing some of the hydrogen atoms from graphane, see Fig. 2(a). The ribbon is formed on one side of the slab only, leaving the graphane layer on the other side intact. We have relaxed the ribbon atoms, the CH rows on the edges of the ribbon, and the two topmost substrate atoms below it. The relaxation of further CH rows or substrate layers does not affect the results. The supercell used in the calculations was from four to nine graphane unit cells in the ribbon transverse direction in order to avoid interaction of the periodic images, the pristine graphane region between adjacent graphene strips always being wider than the ribbon width. Both antiferromagnetic (AFM) and ferromagnetic (FM) initial spin configurations were considered, and compared to the nonmagnetic case. In order to facilitate the convergence of the spin-polarized calculation, an AFM initial guess was obtained by using the spin configuration of a freestanding graphene ribbon in graphane. As freestanding one-sided graphane was not found stable, double-sided graphane in the chair configuration was used. Ribbons with an odd number of zigzag lines were found to bind to the substrate on one of the edges, leading to localized states near the Fermi energy and absence of a ZGNR-like band structure.

The 4, 6, and 8 zigzag chains wide ribbons were studied and as a representative example, the relaxed structure of a six-chain zigzag ribbon is shown in Fig. 2. For clarity,

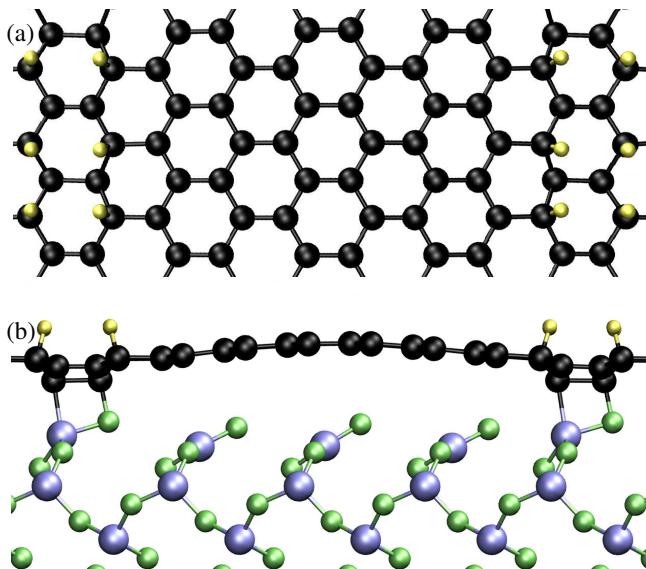


FIG. 2. (Color online) The six zigzag chains wide graphene ribbon in graphane on the SiO_2 substrate. The visualization does not correspond to the calculational unit cell. (a) Top view showing the hydrogen atom configuration with respect to the graphene layer, substrate atoms omitted for clarity. (b) Side view showing the bonding of graphane to substrate and the curvature of the graphene ribbon. The colors are as in Fig. 1.

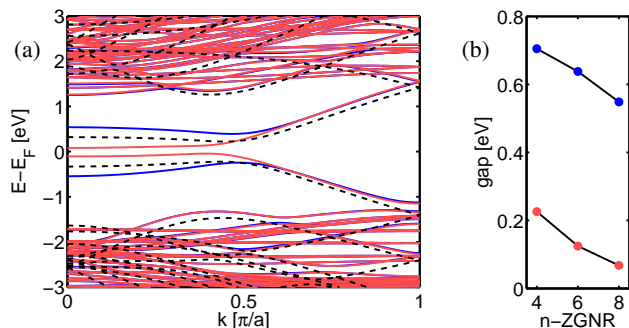


FIG. 3. (Color online) (a) The band structure of the antiferromagnetic 6-ZGNR. The dashed lines show the spin-degenerate bands for the same ribbon in double-sided graphane without substrate. Blue (dark) and red (gray) correspond to the two spin orientations that are non-degenerate only near E_F . (b) The band gaps as a function of the ribbon width for both spin orientations.

the substrate is removed from the top view in Fig. 2(a). Although the carbon-carbon bond length in the ribbon is shorter than that of graphane (1.441 Å compared to 1.487 Å, respectively) the planarity of graphene together with the longer equilibrium distance from the substrate causes the graphene ribbon to bend slightly, see Fig. 2(b). The narrow ribbons have more strain. The Si and O atoms below the ribbon are displaced by approximately 0.3-0.6 Å from the positions corresponding to the opti-

mized SiO_2 -graphane interface.

States with both AFM and FM spin order were found and like in the absence of the substrate [4], the AFM was lower in energy. For example, the energy difference between these two states was 25 meV per edge carbon atom for 4-ZGNR corresponding to a temperature of 290 K. The nonmagnetic state was found to lie yet higher in energy, the difference to the AFM state being 41 meV per edge atom.

Fig. 3(a) shows the band structure for the AFM 6-ZGNR. The spin density within the ribbon area is analogous to that of freestanding nanoribbons [4], the two edges having opposite spin orientations and the two sublattices being antiferromagnetically coupled. The hydrogen atoms at the interface are spin-polarized to the same spin direction as the outermost carbon atoms of the ribbon. In Fig. 3(a), also the band structure for a GNR in free-standing double-sided graphane is shown in dashed lines. The substrate bands slightly squeeze the ribbon bands together but, more importantly, in the presence of the substrate, the spin degeneracy is broken and the spin species have gaps of unequal magnitude. The change of the band structure of a ZGNR towards half-metallicity has previously been predicted to be induced by an external electric field [3–5], boron and nitrogen doping [7, 8] and asymmetric terminating groups on the two edges of the ribbon [3, 6]. In this case, however, none of these factors is present and the effect is given by the asymmetric coupling of the ribbon edges to the substrate, the inversion symmetry between the edges of the ribbon being broken. Although the highest occupied Kohn-Sham orbitals are mostly localized at the ribbon, some density is found around the uppermost oxygen atoms near the ribbon edge. The asymmetry of these oxygens leads then to the broken spin and charge symmetries seen in the band structures. As some of the charge density in the spin-polarized states has moved onto the substrate, the ribbon is slightly doped. In calculations using the Hubbard model, doping has been predicted to lead to analogous band structures [29]. The indirect spin-polarized band gaps of the AFM ribbons decrease monotonically as a function of the ribbon width, see Fig. 3(b).

To conclude, we have presented the two lowest-energy graphane configurations on oxygen-terminated silicon dioxide substrate with quarter and half hydrogen coverage of the graphene carbons and subsequently formed graphene nanoribbons in the half-hydrogenated structure. The presence of the SiO_2 substrate has shown to substantially change properties of the graphene nanoribbons embedded in graphane. More specifically, the asymmetry introduced by the substrate structure breaks the spin degeneracy of the antiferromagnetically ordered ribbons introducing spin-asymmetry in the gap. Apart from that, these zigzag nanoribbons resemble the freestanding ribbons showing antiferromagnetic spin order between the ribbon edges and relatively flat bands close to the

edge of the Brillouin zone. In technological applications, such systems that could be turned to half-metallic could provide a spin-polarized current and function as spin filters. Recently, the stability of zigzag-edged GNRs has been questioned as in freestanding ribbons, the edge is susceptible to reconstructions and hydrogen adsorption [21, 22]. In our system, the ribbon edge is fully saturated by graphane, and such reconstructions are unlikely. Thus, dehydrogenation could serve as a route to magnetism in GNRs.

Finally, even if hydrogenating graphene evenly and in a stable manner is currently experimentally challenging, very recent experimental and theoretical studies [30–33] have shown that stoichiometrically fluorinated graphene is stable, insulating, with properties similar to those of graphane. To our knowledge, selective defluorination of graphene fluoride has not yet been experimentally demonstrated. Theoretical calculations [34] predict that the properties of ribbons obtained by defluorination should be very similar to those obtained by dehydrogenation. We thus expect the surface-induced spin-asymmetry to be observable also in graphene fluoride-based ribbons.

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* mari.ijas@aalto.fi

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